A STUDY OF THE INTRODUCTION OF IONS INTO THE REGION OF STRONG FIELDS WITHIN A QUADRUPOLE MASS SPECTROMETER

by

Wilson M. Brubaker

ABSTRACT

Experiments with the round and the hyperbolic quadrupole units have been continued. The preliminary data which were obtained previously have been substantiated. The resolving power of the hyperbolic quadrupole is about twice that of the round at comparable sensitivities. Resolving power of 600, measured at the 10% peak height, was obtained with the hyperbolic unit at a transmission efficiency of 20%, when excited at very low power. At higher power, a resolving power of 1000 was obtained at 10% transmission efficiency. Flat-topped peaks were observed at resolving powers below 400.

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INTRODUCTION

This report covers the work done by the Bell & Howell Research Center on NASA Contract NASW-1298 from 17 February through 17 May, 1967. This is the seventh quarter of the Contract.

This project is concerned with the introduction of ions into the region of strong fields in the quadrupole mass filter, and with the comparison of the performances of quadrupole structures with round and with hyperbolic field-forming surfaces.

During this quarter additional data have been obtained which compare the operation of the two quadrupoles. The superior performance of the hyperbolic rods is now well established.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus is the same as that described in last quarter's report, with the exception that an electrometer amplifier and a X-Y recorder have been used as read-out devices in place of the oscillograph. The only change in the experimental procedure is that associated with the change in the read-out devices used.

As before, the krypton spectrum was used for these tests. The sensitivity as a function of resolving power is again used to display the performance of the instruments.

EXPERIMENTS

The prime objective during this quarter was the comparison of the operation of the two quadrupoles, one with round and the other with hyperbolic surfaces. Data were obtained which indicate these comparisons when the quadrupoles were operated in the delayed dc ramp mode.

Two sets of experiments were performed. In one, the number of cycles of radio frequency which occur during the ion transit was held constant while the excitation frequency was varied over a factor of two. The ion energy varied by a factor of four, and the power required to excite the system varied about 30 times! In the other set of experiments, the ion energy remained low while the excitation frequency was again varied over the two-to-one range. Under these conditions exceptional resolving power at high transmission efficiency was obtained with the hyperbolic quadrupole.

QUADRUPOLE PERFORMANCE DATA

In the first set of experiments the number of radiofrequency cycles which occur while the ions traverse the filter is 110. For the round rod quadrupole, this should give a resolving power of 475, according to the semi-empirical formula given by Paul. The excitation frequencies were 0.707, 1.0, and 1.414 MHz, and the corresponding ion injection energies were 1, 2, and 4 volts.

Data comparing the performance of the round and the hyperbolic units are presented in Figures 2, 3, and 4. In each case the sensitivity of the hyperbolic unit was arbitrarily set at 100%. The response of the round unit, operating under the same conditions, is given in its relation to that of the hyperbolic. The sensitivity of the round unit is consistently lower than that of the hyperbolic, even at unit resolving power. This difference is not found in the sources. Interestingly (and unanticipatedly) the difference at the lowest resolving power increases with excitation frequency.

In the comparison of the data in the three figures, the variation in the output of the ion source as a function of ion energy as displayed in Figure 1 should be kept in mind. The data as presented here are normalized to the sensitivity of the hyperbolic unit, and do not indicate the relative sensitivities of the instruments when operated at the different frequencies. This manner of presenting the data is chosen to emphasize the differences in the performances of the round and the hyperbolic quadrupoles when they are operated in identical manners.

If all of the potentials in the units were scaled in proportion, the data of the three figures should all be alike. That they are different indicates that some of the potentials did not vary in the same proportion. In the operation of the instruments the sources were adjusted for maximum output of unresolved ion current at each level of ion energy. Unfortunately, this did not occur at proportional voltages on the ion focus electrode in the ion source. However, it is most probable that there were other and more important potentials which did not vary in proportion. In particular, there are the potentials in the ion source which result from the space charge of the electron beam. In addition, there may have been insulating surfaces which resulted from extensive ion bombardment.

The data of Figure 2 are of particular interest. Here the excitation frequency was only 0.707 MHz, and the maximum ac potential on the rods was only 130 volts at mass 86! Even so, the performance of the hyperbolic rods is very impressive. A resolving power of 500 is obtained at a sensitivity which is 44% of that observed at low resolving power.

The most significant factor in the comparison of the two quadrupoles is the resolving power observed at constant sensitivity. On this basis, the hyperbolic quadrupole outperforms the round by a factor of two! When it is recalled that the only known difference between the two units is the shape of the rods the confidence in the data is excellent. Further, as mentioned in the last report, the data were not altered when the rods were interchanged in the two vacuum envelopes. The sources and detectors remained with their original envelopes.

In the second set of experiments, the ion energy was held at one volt and the excitation frequency varied. As expected, the resolving power increased as the frequency was raised. These data are presented in Figure 5. The normalization is to the hyperbolic sensitivity at each of the two excitation frequencies. Again, the resolving power of the hyperbolic exceeds that of the round by a factor of two for comparable sensitivities. Flat-topped peaks are obtained with the hyperbolic to a resolving power of about 400. At a resolving power of 1000 the transmission efficiency is down only to 10%. Figure 6 shows a series of scans over the mass 84 peak as the resolving power was varied. Most quadrupole peaks are asymmetrical. In the conventional mode of operation, the high mass side of the peaks have the steeper slope. That this should be so is seen by referring to the stability diagram and noting that the scan line crosses the y-stability limit obliquely, and the x-stability limit nearly normally. In the delayed dc ramp mode of operation, the slope is steeper on the low mass side of the peak. This change must be due to the avoidance of the y-unstable condition at the entrance to the quadrupole.

CONCLUSIONS

The experimental work done during this quarter has compared the performance of the round and the hyperbolic quadrupoles. In every instance the resolving power of the hyperbolic has been found to exceed that of the round by about a factor of two, for similar sensitivities. With the hyperbolic quadrupole, operated in the delayed dc ramp mode, a resolving power of 1000 at the 10% point has been obtained with a transmission efficiency of 10%.

NEXT QUARTER'S ACTIVITIES

During the next quarter the data will be refined and the sensitivities will be placed on an absolute scale. Theoretical and experimental work will be done on the ion source, with a goal of obtaining higher sensitivity at the lower ion energies.

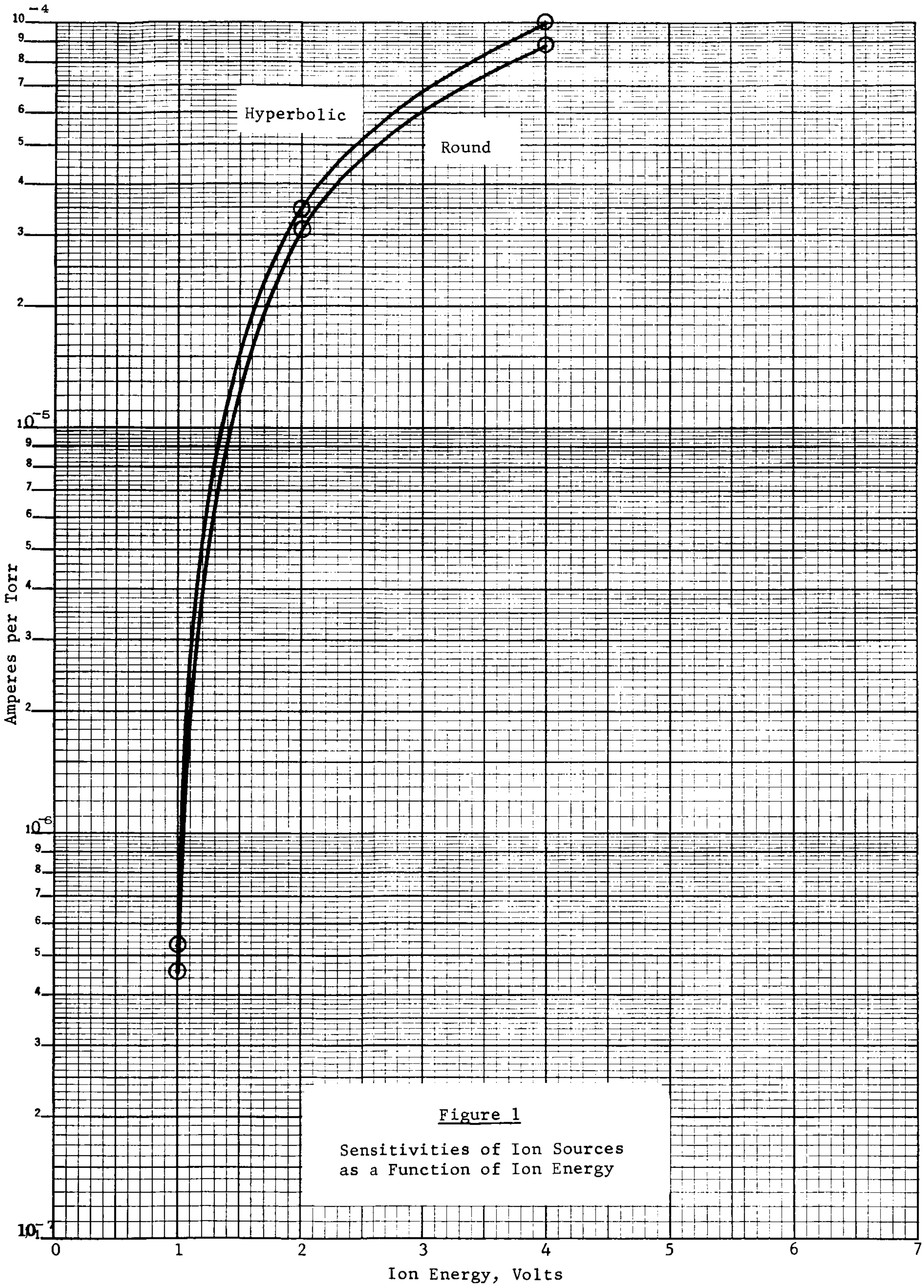


Figure 1

Sensitivities of Ion Sources as a Function of Ion Energy

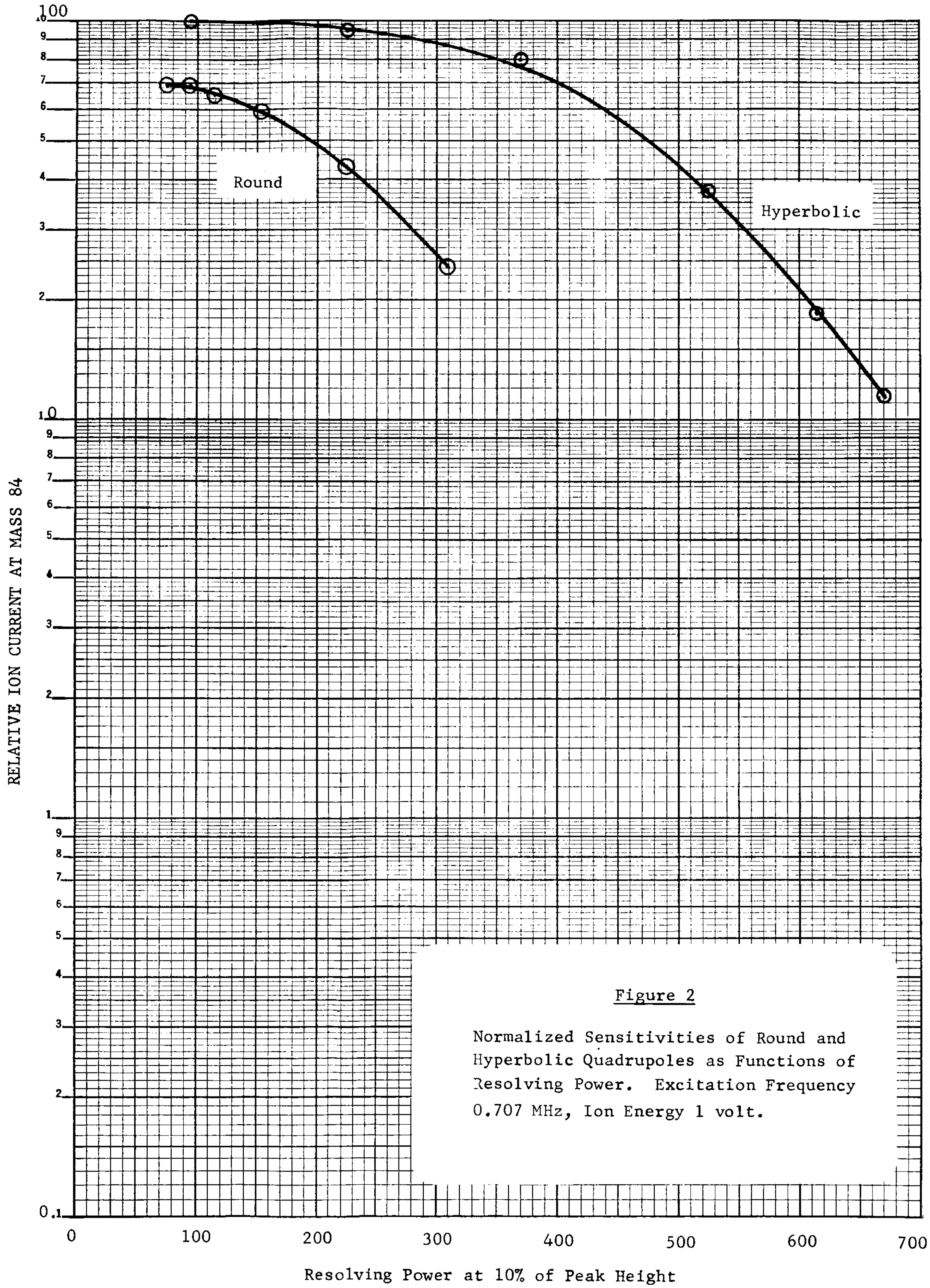


Figure 2

Normalized Sensitivities of Round and Hyperbolic Quadrupoles as Functions of Resolving Power. Excitation Frequency 0.707 MHz, Ion Energy 1 volt.

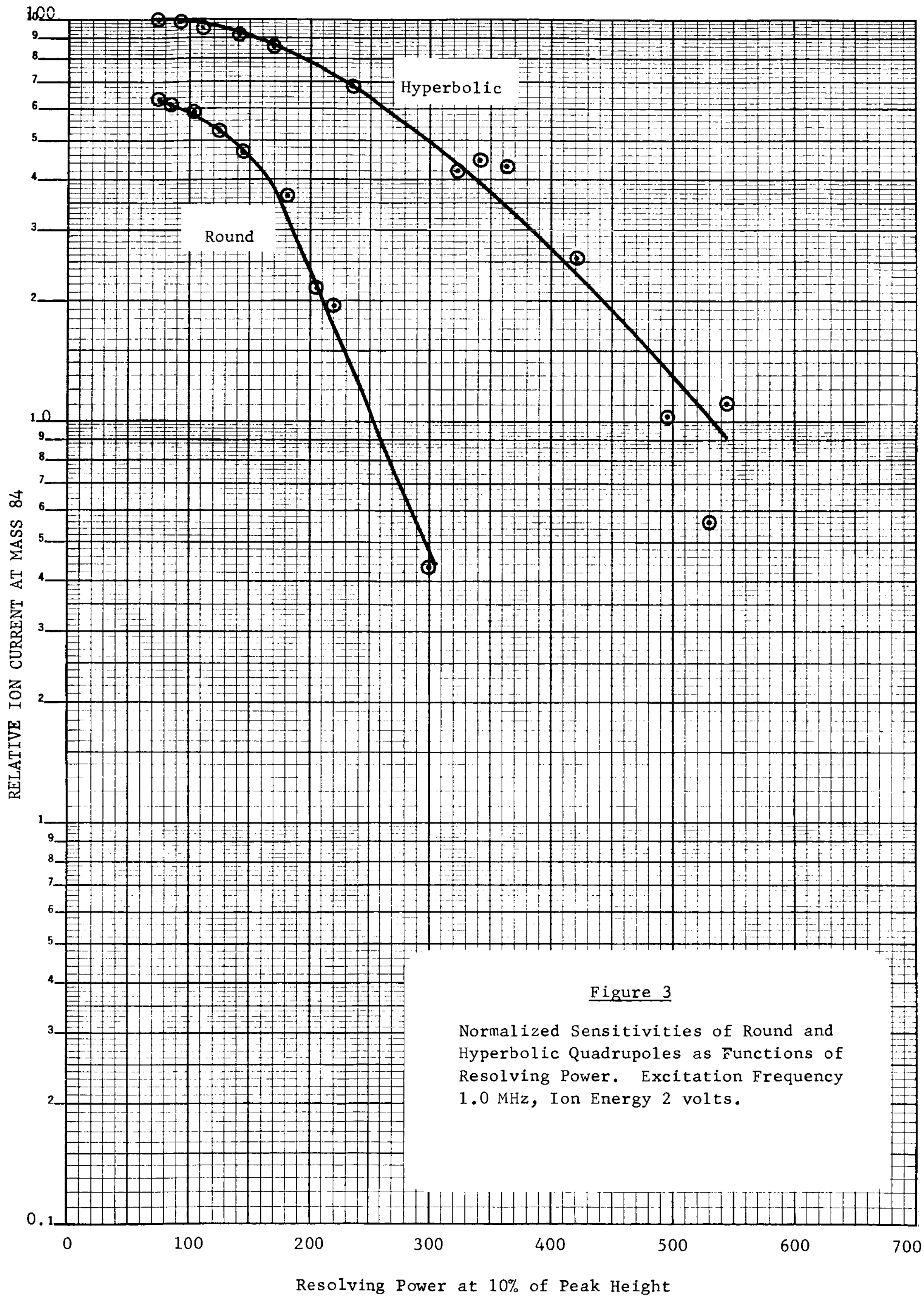
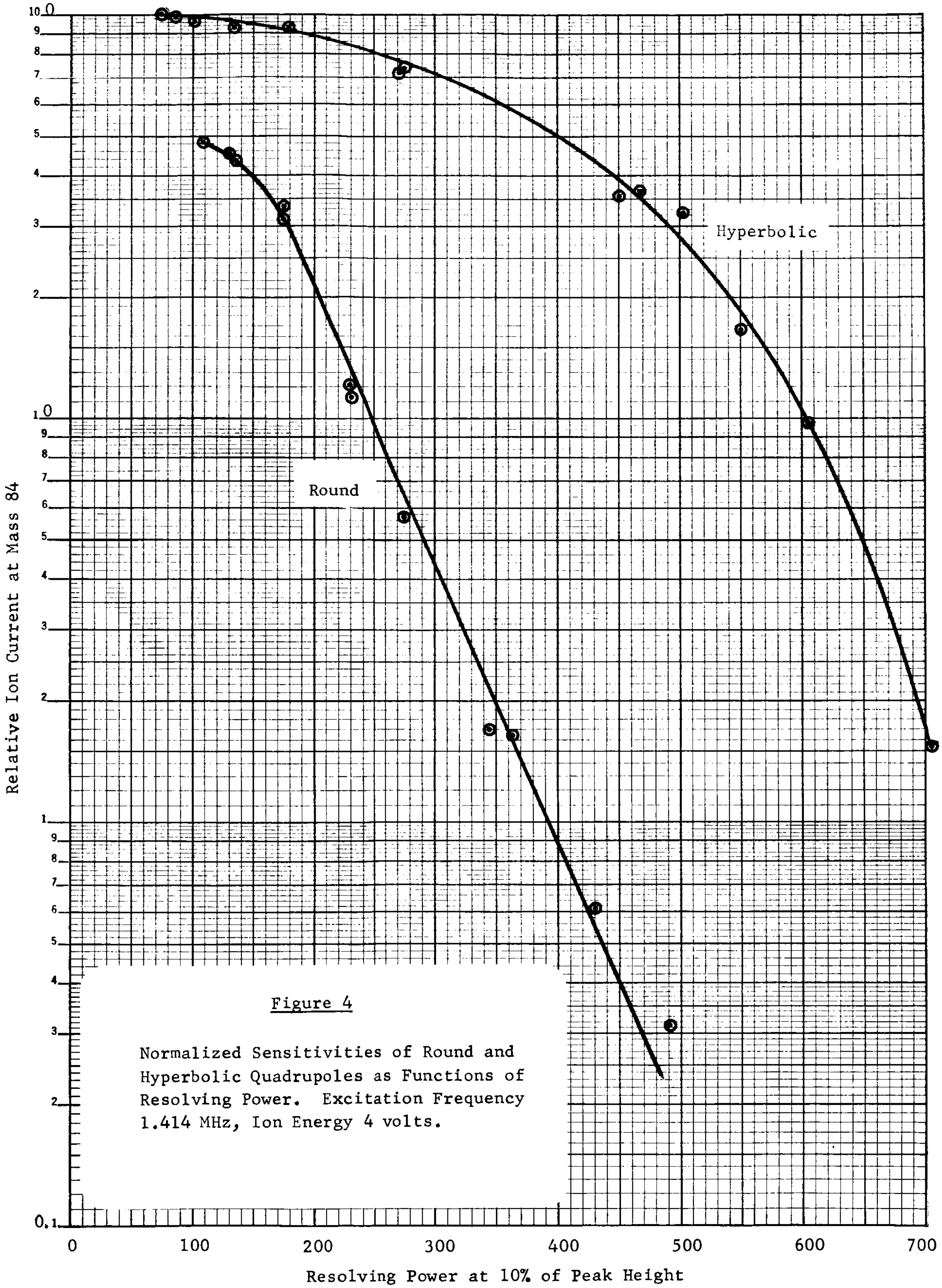


Figure 3

Normalized Sensitivities of Round and Hyperbolic Quadrupoles as Functions of Resolving Power. Excitation Frequency 1.0 MHz, Ion Energy 2 volts.



<u>Figure 4</u>

Normalized Sensitivities of Round and Hyperbolic Quadrupoles as Functions of Resolving Power. Excitation Frequency 1.414 MHz, Ion Energy 4 volts.

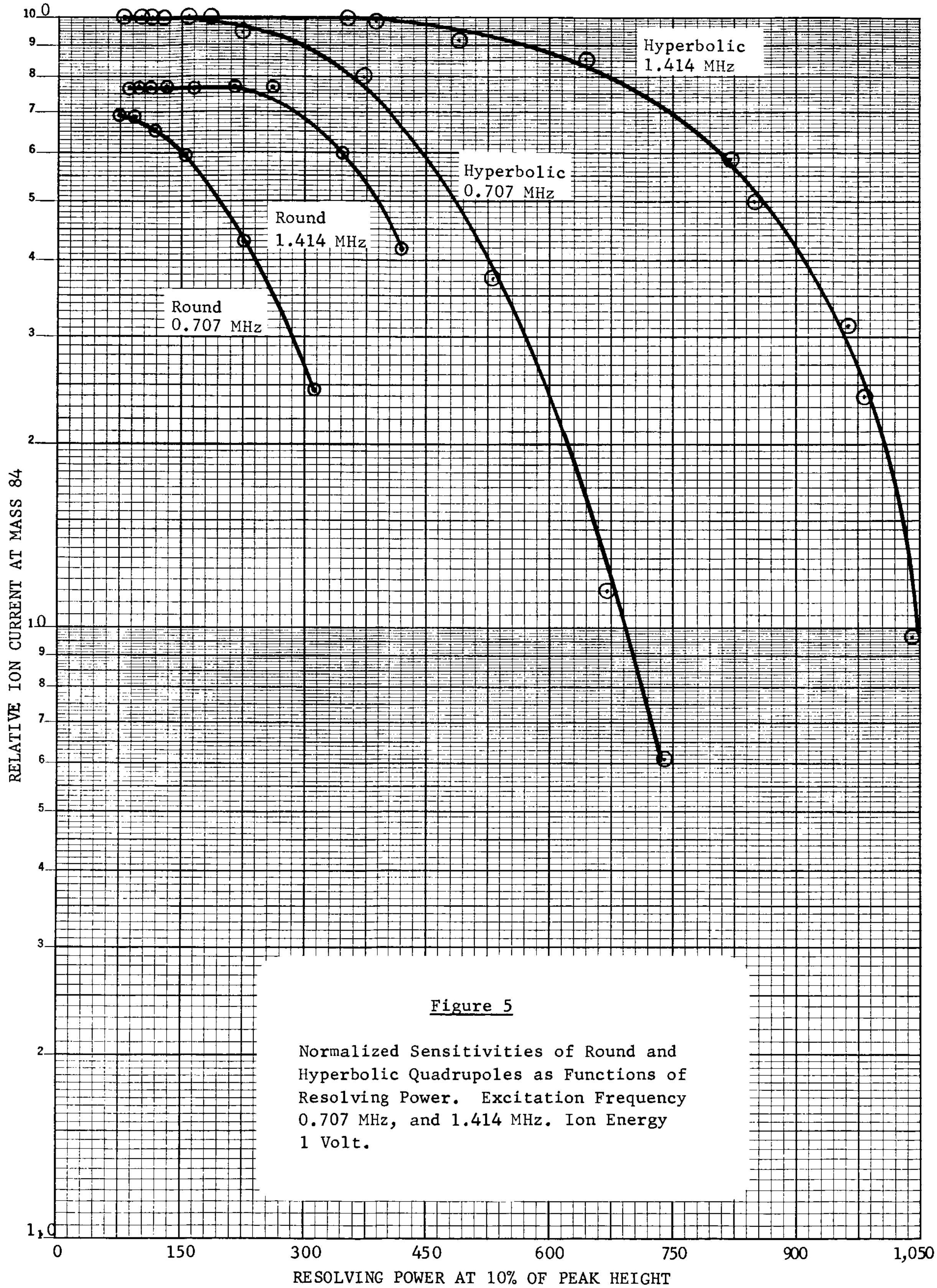


Figure 5

Normalized Sensitivities of Round and Hyperbolic Quadrupoles as Functions of Resolving Power. Excitation Frequency 0.707 MHz, and 1.414 MHz. Ion Energy 1 Volt.

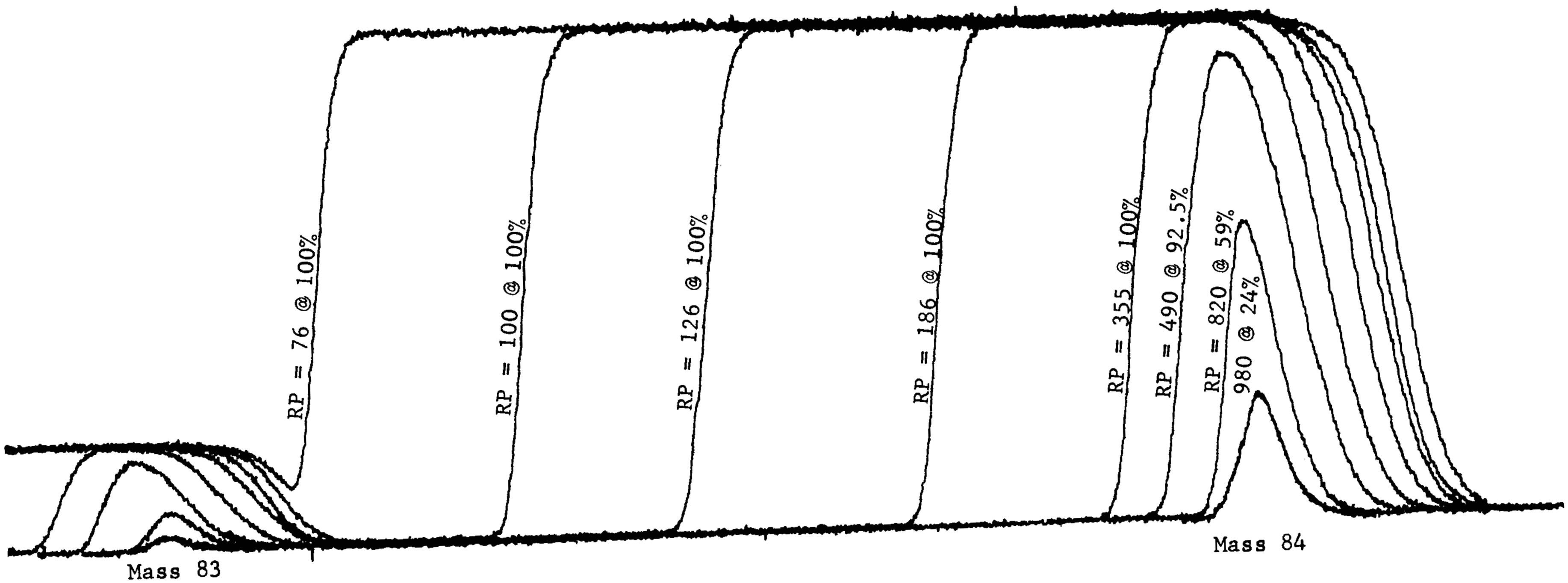


Figure 6

Multiple Scans of Mass 84 Peak at Various Resolving Powers.
Excitation Frequency 1.414 MHz; Ion Energy 1.0 Volt.

APPENDIX

I

A paper, entitled "The Efficient Introduction of Ions Into a Quadrupole Mass Filter" was presented at the Fifteenth Annual Conference on Mass Spectrometry and Allied Topics in Denver, May 14-19, 1967.

Manuscript accepted for inclusion in Proceedings of Fifteenth Annual Conference on Mass Spectrometry and Allied Topics, Denver, May 14-19, 1967

THE EFFICIENT INTRODUCTION OF IONS INTO A QUADRUPOLE MASS SPECTROMETER*

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ABSTRACT

The efficiency with which ions are introduced into a quadrupole mass filter is increased by several powers of ten by the appropriate control of the fields at the entrance to the filter. This is accomplished by using an additional set of four electrodes. The potentials applied to these additional electrodes have a smaller ratio of dc to ac values than the potentials applied to the quadrupole. Computer studies reveal the high vulnerability of the entering ions to the impulses which they receive as they traverse the fringe fields of the conventional quadrupole. Further studies with the computer reveal the effectiveness of the altered fields in eliminating these undesired impulses. Experimental data compare the operation of the quadrupole with and without use of the additional electrodes. It is found that the sensitivity of the instrument can be increased by powers of ten without degrading the resolving power through the use of these auxiliary electrodes.

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It has long been recognized that there is a direct relationship between the resolving power of the quadrupole and the number of cycles spent by the ions in traversing the device. Increasing the frequency of excitation and decreasing the axial velocity both increase the transit time in periods of the ac excitation. The former is accomplished only at a great expense in power, and the latter with a decrease in sensitivity. The severe attenuation of the transmission of ions through the quadrupole which results from directing ions toward the instrument at low velocity occurs because the ions receive a large component of radial velocity as they traverse the fringing fields.

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* This research was supported in whole or in part by the National Aeronautics and Space Administration under Contract No. NASW-1298, monitored by Dr. Donald P. Easter.

Through an alteration of the relative strengths of the dc and the ac fields at the entrance to the quadrupole it is possible to avoid the severe loss of low velocity ions. This alteration of the fields is accomplished through the use of an additional set of four electrodes in the vicinity of the entrance aperture.[1] This refinement in the quadrupole significantly decreases the size of the instrument and the required power for a given resolving power. These considerations are particularly important for space applications.

The usual use of the stability diagram is to indicate the manner in which the mass spectrum is produced. In this discussion it is used to help understand what happens to an ion as it passes through the fringe fields while entering the quadrupole. As an ion enters the quadrupole on a path which is parallel to the instrument axis, the values of both a and q vary from zero to full value. For ions which are transmitted through the quadrupole at high resolving power the locus of the working point lies very close to the apex of the stability diagram while the ion is within the quadrupole. During almost all of the transit of the ion through the fringe fields, the working point lies far above the y-stability limit. Here the acceleration is directed away from the instrument axis.

If the path of the working point as the ion enters the quadrupole can be made to lie within the stable portion of the stability diagram, the undesired y-directed impulse can be avoided. This desired situation can be achieved if the working point moves first along the q-axis as it leaves the origin. Such motion is obtained if the field-forming surfaces adjacent the entrance aperture are excited with ac potentials only. These additional electrodes lie between the entrance aperture and the usual quadrupole rods which are excited with their normal amounts of ac and dc potentials. Because the dc fields are delayed (along the instrument axis), this mode of operation has been termed "delayed dc ramp".

Experiments were made in which eight-volt ions were injected into a ten-inch quadrupole operating at 1.6 MHz. Direct comparison of the operation in the conventional and the delayed dc ramp modes were made. At the modest resolving power of 100 the sensitivity of the delayed dc ramp mode was 50 times that of the conventional. At a resolving power of 400 this difference becomes 250.

In the conventional quadrupole, as has just been shown, the use of low injection energy increases the number of cycles spent by the ions in traversing the fringe fields and causes severe attenuation of the transmission efficiency. Conversely, if high transmission efficiency is obtained by using higher ion injection energies, then the upper limit of the resolving power is reduced.

In the improved quadrupole, operating in the delayed dc ramp mode, ions can be introduced at low energies without causing the transmission efficiency to be low. Thus high resolving power at high sensitivity can be achieved.

REFERENCES

[1]W. M. Brubaker, "Auxiliary Electrodes of Quadrupole Mass Filters," U. S. Patent 3,129,327.

A more detailed paper will be published in "Advances in Mass Spectrometry," Volume 4, (Proceedings of International Mass Spectrometry Conference, Berlin, September, 1967).

Manuscript accepted for presentation at the Mass Spectroscopy Conference in Berlin, September 25-29, 1967, and for publication in "Advances in Mass Spectrometry," Volume 4.

IMPROVED QUADRUPOLE*

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ABSTRACT

Experimental data reveal that the sensitivity of the conventional quadrupole can be increased by a factor of ten to one-hundred with no sacrifice in the resolving power. This is accomplished through the use of a set of four additional electrodes at the ion entrance end of the mass filter. As an ion traverses the fringe fields of a conventional quadrupole the working point moves through the y-unstable portion of the stability diagram. Under these circumstances, computer studies have shown that the ion receives a large impulse in the y-direction. By appropriately energizing the auxiliary electrodes of the improved quadrupole, it is possible to have the working point remain within the x- and y-stable portion, and thus to avoid the undesirable radial impulse. The results of computer studies and experimental data are presented.

INTRODUCTION

The quadrupole mass filter is uniquely different from most other mass analyzers. Its maximum dimension is along the axis, yet the fields within the structure have no component in this direction. Additional length of the instrument serves merely the purpose of increasing the time spent by the ions in traversing the analyzer. It has long been recognized[1] that there is a direct relationship between the resolving power of the quadrupole and the number of cycles spent by the ions in traversing the device. Increasing the frequency of excitation and decreasing the axial velocity both increase the transit time measured in periods of the ac excitation. The former is accomplished only at a great expense in driving power, and the latter results in a decrease in sensitivity. The severe attenuation of the transmission of ions through the quadrupole which results from

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directing ions into the instrument at low velocity occurs because the ions receive a large component of radial velocity as they traverse the fringing fields.

Through an alteration of the relative strengths of the dc and the ac fields at the entrance to the quadrupole it is possible to avoid the severe loss of low velocity ions.[2] This alteration of the fields is accomplished through the use of an additional set of four electrodes in the vicinity of the entrance aperture. This refinement in the quadrupole significantly decreases the size of the instrument and the required driving power for a given resolution. These considerations are particularly important for space applications.

THEORY

General discussion of the theory of the quadrupole mass filter requires reference to the stability diagram, shown in Figure 1. The coordinates are the dimensionless numbers a and q. For a given ratio of the dc to the ac potentials, the "working point" for ions of all values of m/e fall on a straight line which passes through the origin. This is denoted as the "scan line".

The usual use of the stability diagram is to indicate the manner in which the mass spectrum is produced. In this discussion it is used to help understand what happens to an ion as it passes through the fringe fields while entering the quadrupole. First, it should be noted that the dimensionless variables a and q are proportional to the fields at a given position in the plane transverse to the instrument axis. Thus, as an ion enters the quadrupole on a path which is parallel to the instrument axis, the values of both a and q vary from zero to full value. For ions which are transmitted through the quadrupole at high resolving power the locus of the working point must lie very close to the apex of the stability diagram while the ion is within the quadrupole.

Theory previously developed[3] shows that the radial acceleration experienced by an ion as it responds to the combined dc and ac fields is proportional to the vertical distance between the y-stability limit and the working point. The working point in the quadrupole for a transmitted ion lies very near to the apex, just under the y-stability limit, and the net acceleration is directed toward the instrument axis. But during almost all of the transit of the ion through the fringe fields, the working point lies far above the y-stability limit. Here the acceleration is directed <u>away</u> from the instrument axis. Computations have shown that the magnitude of the y-directed momentum impulse which the ion receives as it traverses the fringe fields varies <u>exponentially</u> with the number of periods (cycles) of ac excitation which occur during its transit. Thus it is seen that the number of cycles spent by the ions in the fringe fields must be kept quite small, unless there is to be an acute attenuation of the transmission of ions through the instrument.

If the path of the working point can be made to lie within the stable portion of the stability diagram while the ions are passing through the fringing fields, the undesired y-directed impulse can be avoided. This desired situation can be achieved if the working point moves first along the q-axis as it leaves the origin. Such motion is obtained if the field-forming surfaces adjacent the entrance aperture are excited with ac potentials only. These additional electrodes lie between the entrance aperture and the usual quadrupole rods which are excited with their normal amounts of ac and dc potentials. Because the dc fields are delayed (along the instrument axis), this mode of operation has been termed "delayed dc ramp". One of the many paths the working point may take through the stability diagram in the delayed dc ramp mode of operation is denoted as a "preferred path" in Figure 1.

COMPUTER STUDIES

The purpose of the computations was to evaluate the seriousness of permitting the working point to move through the y-unstable portion of the diagram as the ions traverse the fringe fields of the conventional quadrupole. Computations were made in which the ions were assumed to be formed within the quadrupole, to enter a conventional quadrupole with coincident (normalized) dc and ac ramps, and to enter the improved quadrupole, in the delayed dc ramp mode.

Computer studies differ from laboratory studies in that the trajectory is never terminated by the ions striking the rods. The amplitude is limited only by the number of digits in the computer. This was never a concern during these investigations.

The a, q values chosen for the uniform field region correspond to a resolving power of about 400. Further, the working point selected lies very close to the line $\beta_x + \beta_y = 1$, since the envelopes for the x and the y trajectories are nearly identical for this value.

In the first set of calculations the ions were assumed to be formed within the uniform field region, with zero radial velocity, and at the point $x = y = 1$. Since the x and the y forces are completely orthogonal and independent of each other, trajectories for both components of motion were obtained simultaneously. Trajectories were started at 90° phase intervals (of the applied ac potential).

The maximum amplitudes were in general similar for x and y motions, the largest at 90° and 270°, as expected. The amplitudes remained less than 25 times the initial displacement.

In the second set of computations the passage of the ions from regions of zero fields to those of full fields was simulated by causing the magnitudes of the fields (dc and ac) to increase together at a uniform rate from zero to their full values. Computations were again made at the four phase angles, and for ramp lengths of two and ten cycles. In all cases the maximum amplitude for the x-component of motion is less than ten times the initial position, but for the y-component at ten-cycle ramp the normalized amplitudes are all greater than 1000 times the initial displacement! The phase of the ac potential at the start of the computations has little influence on these extremely large amplitudes.

Further computations were made in which the independent variable is the number of cycles which occur while the ions traverse fringe fields. As might have been anticipated, the maximum amplitude varies exponentially with the ramp length, measured in cycles (periods) of ac excitation.

In the third set of computations the ions were assumed to enter the quadrupole in the delayed dc ramp mode. Several different "preferred paths" were used. In the steepest ramp case, the ac fields build up uniformly during the first twelve cycles, the dc field during the second set of six cycles, from the seventh to the twelfth cycle. In all cases, the normalized amplitudes are less than five times the initial displacement.

The results of these computations are summarized in Figure 2. It is seen that the magnitude of the "entrance transient" given the ions is greatly reduced through the use of the delayed dc ramp mode of operation.

EXPERIMENTAL

Apparatus

The additional set of four electrodes at the entrance of the quadrupole has been provided in the form of insulated rod segments, one on each rod. The rod assemblies of the improved quadrupole, and the method used for energizing them are shown schematically in Figure 3. By moving the switch from position A to B, the operation of the quadrupole is changed from conventional to delayed dc ramp modes. The diameter of the rods is 0.6 inches, their length 10 inches. The segments are 0.6 inches long. The excitation frequency was 1.6 MHz.

Results

Krypton gas was used for all observations made in this study. Resolving power measurements were made by observing the width of the mass 84 peak at 10% height and the separation of this peak from the mass 83 peak. Instrument sensitivities are plotted as functions of resolving power at different ion injection energies and for operation in the conventional and the delayed dc ramp modes.

The data obtained at 15-volt ion injection energy are presented in Figure 4. In this instance the resolving power is limited by the transit time of the ions. At this high injection energy the ions traverse the fringe fields in less than three cycles, and the resulting transmission loss is nominal. Even so, the sensitivity in the delayed mode is six times that of the conventional at low resolving powers.

At 8-volt ion injection energy the difference between the conventional and the delayed dc ramp modes of operation is more apparent, as shown in Figure 5. The increased time spent in the quadrupole raises the resolving power very appreciably. However, the greater time spent in the fringe fields of the conventional quadrupole causes a rather severe attenuation of the transmission efficiency. At a resolving power of 100 the instrument sensitivity of the delayed dc ramp mode is 50 times that of the conventional. At a resolving power of 400, this difference becomes a factor of 250!

Four-volt incident ions remain in the system during a large number of cycles of the ac voltage, and the nominal resolving power is high. However, in the conventional quadrupole the sensitivity is too low to be useful because the impulse given the ions in the fringe fields causes them to strike the rods, and be lost. In the dc ramp mode, useful sensitivity is achieved for resolving powers as high as 650. These data are shown in Figure 6.

CONCLUSIONS

In the conventional quadrupole, as has just been shown, the use of low injection energy increases the number of cycles spent by the ions in traversing the fringe fields and causes severe attenuation of the transmission efficiency. Conversely, if high transmission efficiency is obtained by using higher ion injection energies, then the upper limit of the resolving power is reduced.

In the improved quadrupole, operating in the delayed dc ramp mode, ions can be introduced at low energies without causing the transmission efficiency to be low. Thus high resolving power at high sensitivity can be achieved.

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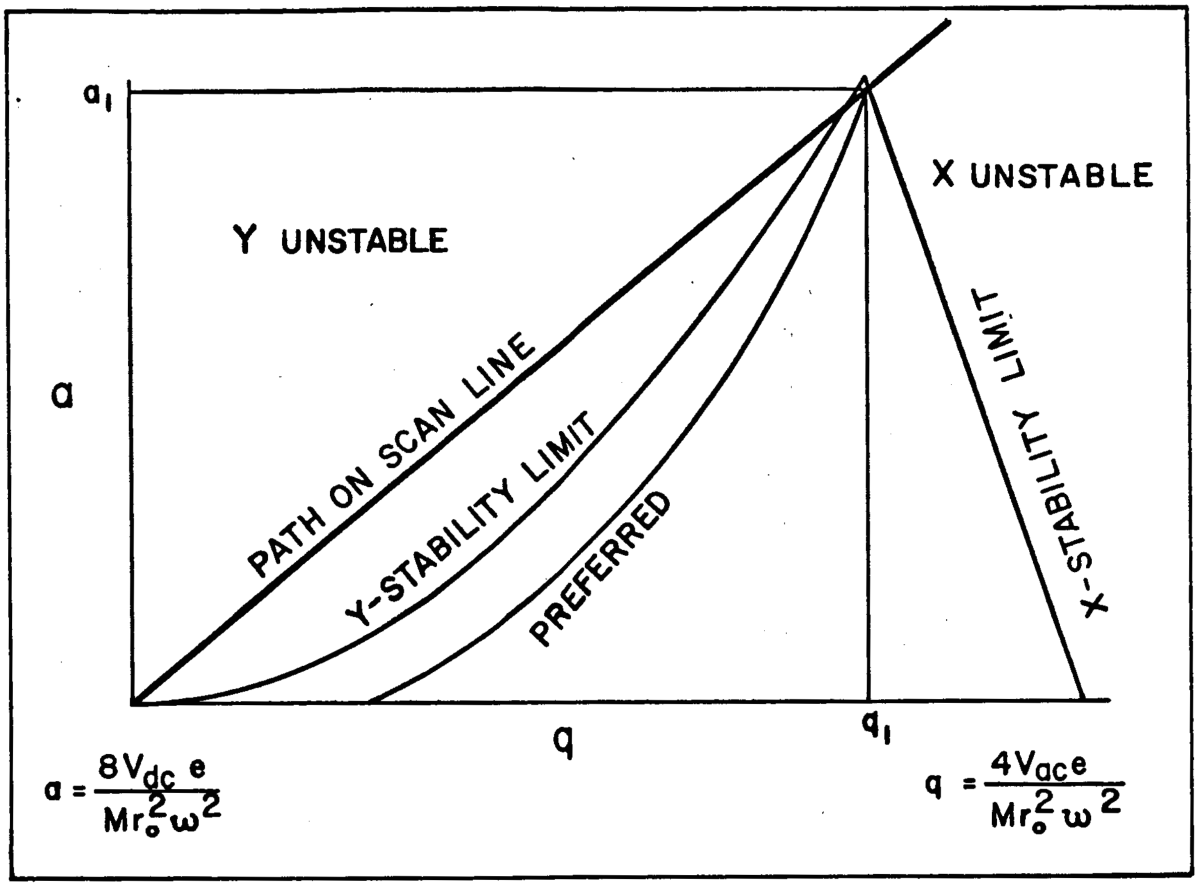
[1] W. Paul, H. P. Reinhard und U. von Zahn, "Das Elektrische Massenfilter als Massenspektrometer und Isotopentrenner," Zeitschrift fur Physik, Bd. 152, S. 143-182 (1958).

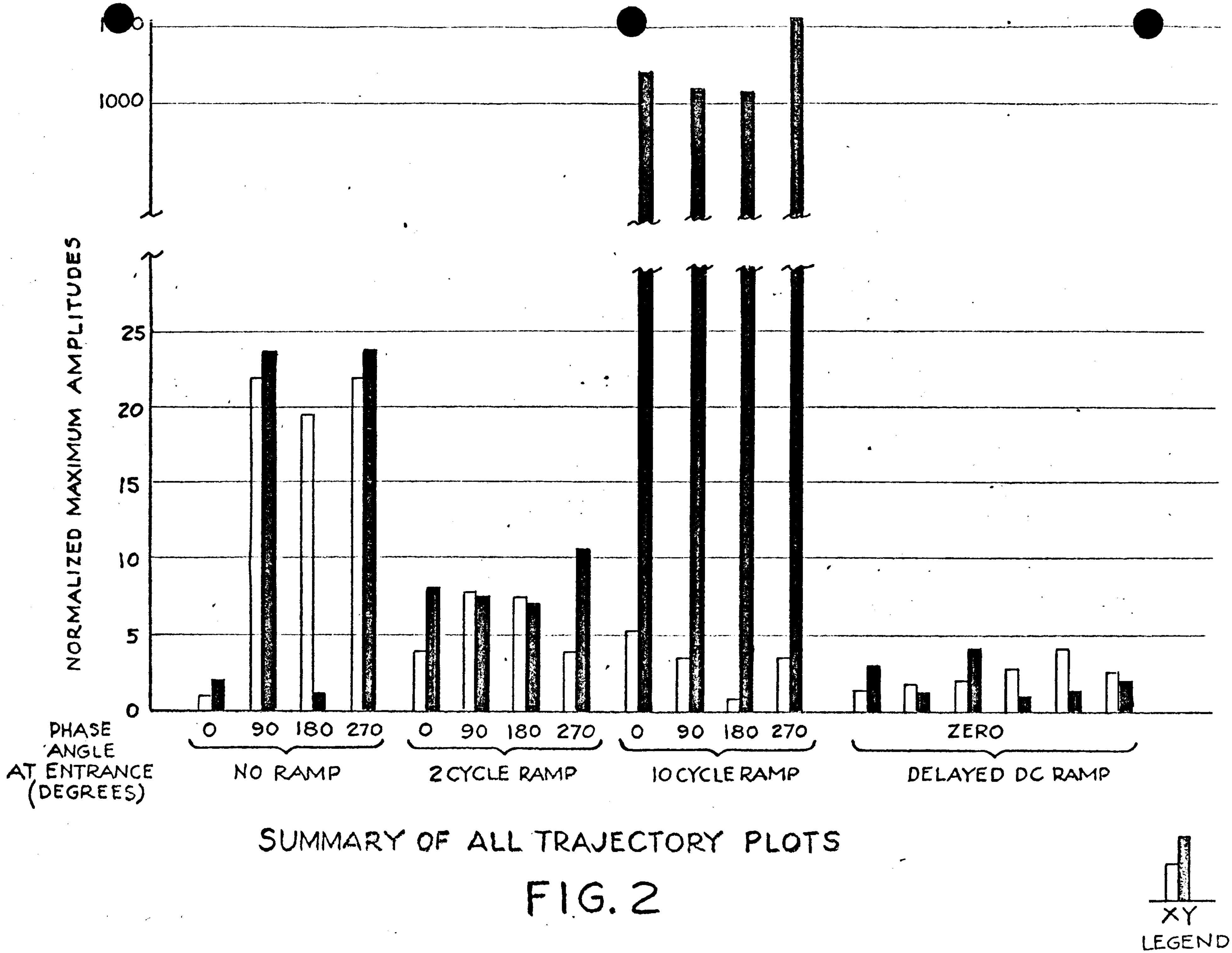
[2] W. M. Brubaker, "Auxiliary Electrodes of Quadrupole Mass Filters," U. S. Patent 3,129,327.

[3] W. M. Brubaker, "The Quadrupole Mass Filter," Paper presented at IX Colloquium Spectroscopicum Internationale, Juin, 1961, Lyon, France. "Study and Development of the Paul-type Mass Spectrometer," Contract No. AF 19(604)-5911, April, 1963.



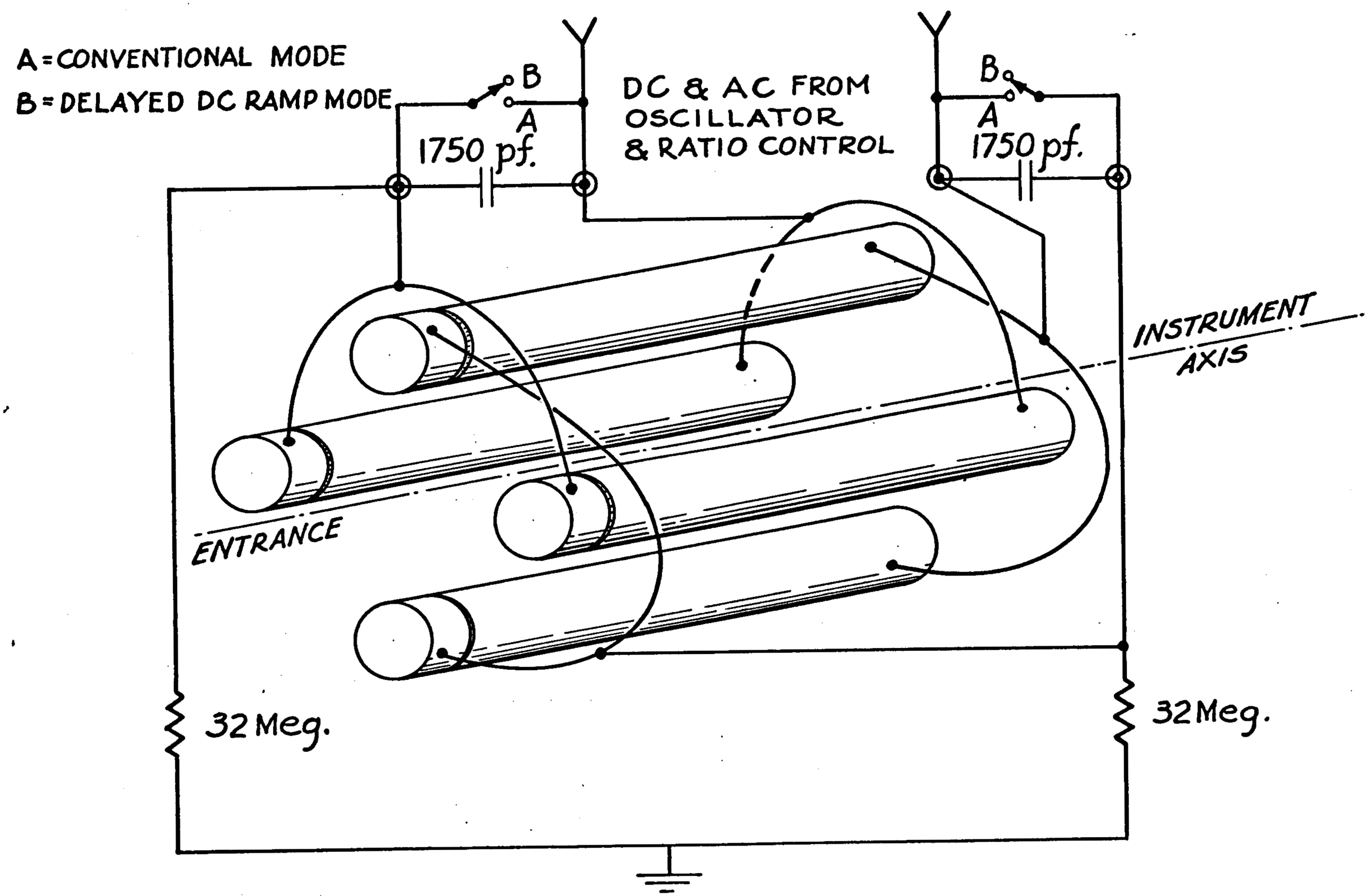
STABILITY DIAGRAM, SHOWING TWO PATHS OF WORKING POINT DURING TRAVERSAL OF FRINGING FIELD.

FIGURE I



SUMMARY OF ALL TRAJECTORY PLOTS

FIG. 2



APPARATUS
FIGURE 3

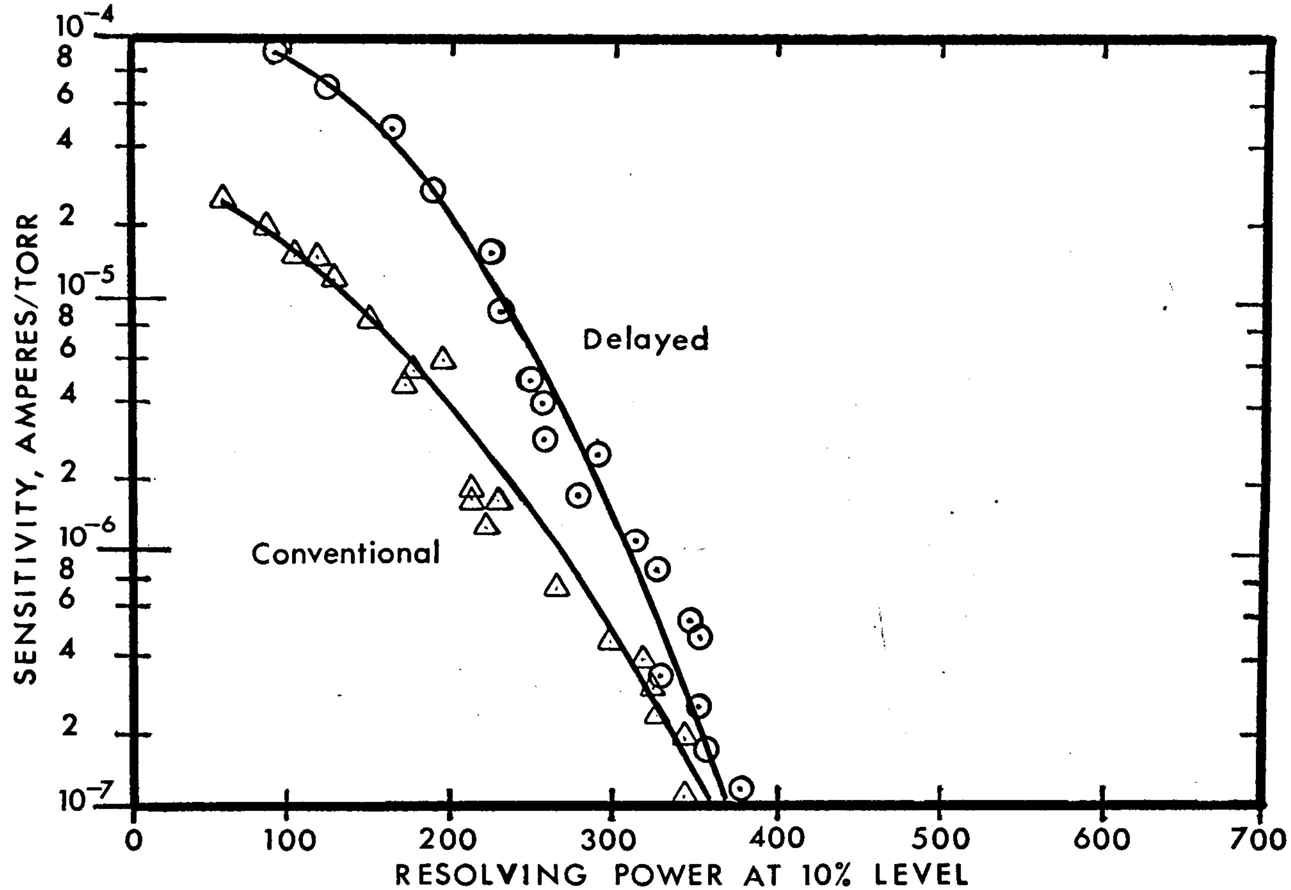


FIGURE 4

SENSITIVITY VS. RESOLVING POWER FOR
CONVENTIONAL AND DELAYED MODES WITH 15-VOLT IONS

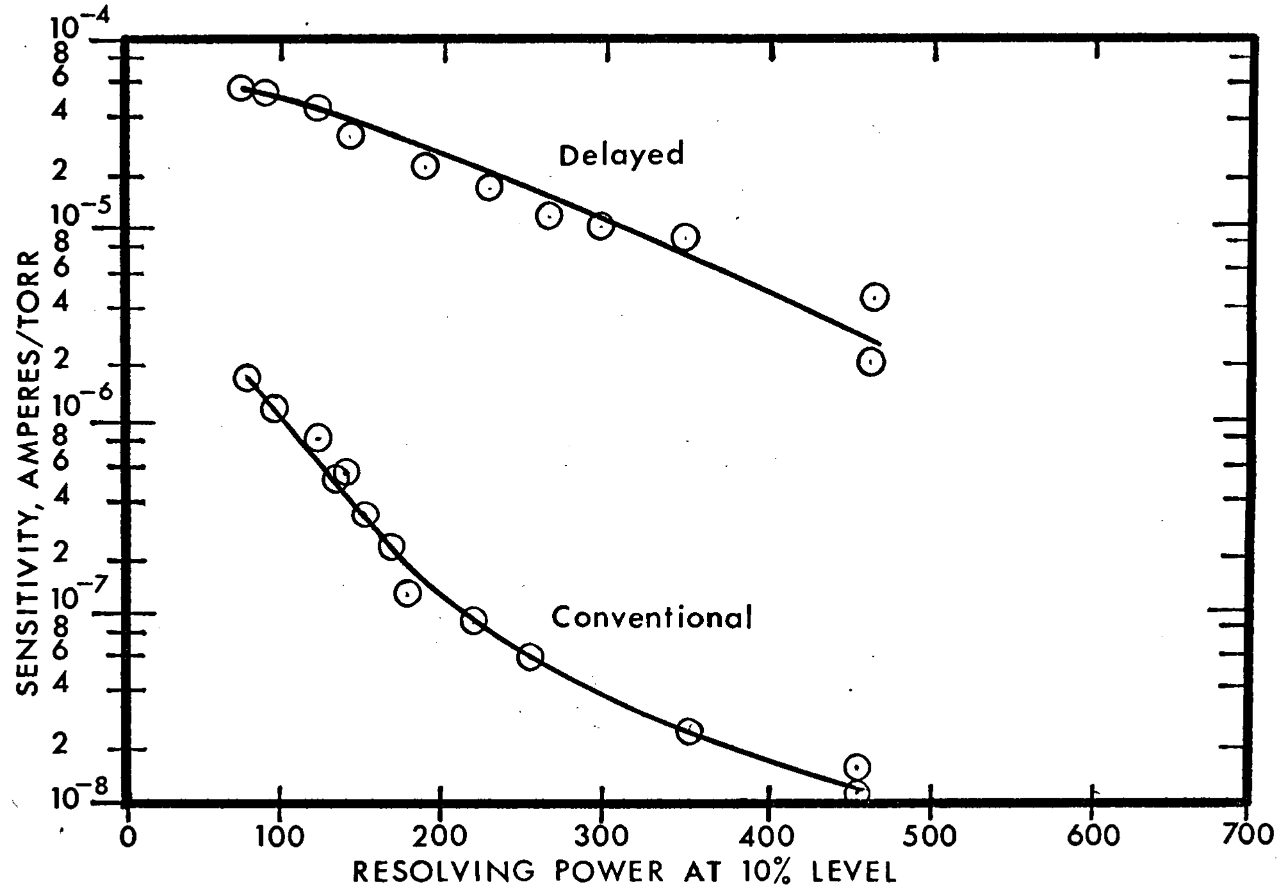


FIGURE 5

SENSITIVITY VS. RESOLVING POWER FOR CONVENTIONAL AND DELAYED MODES WITH 8-VOLT IONS

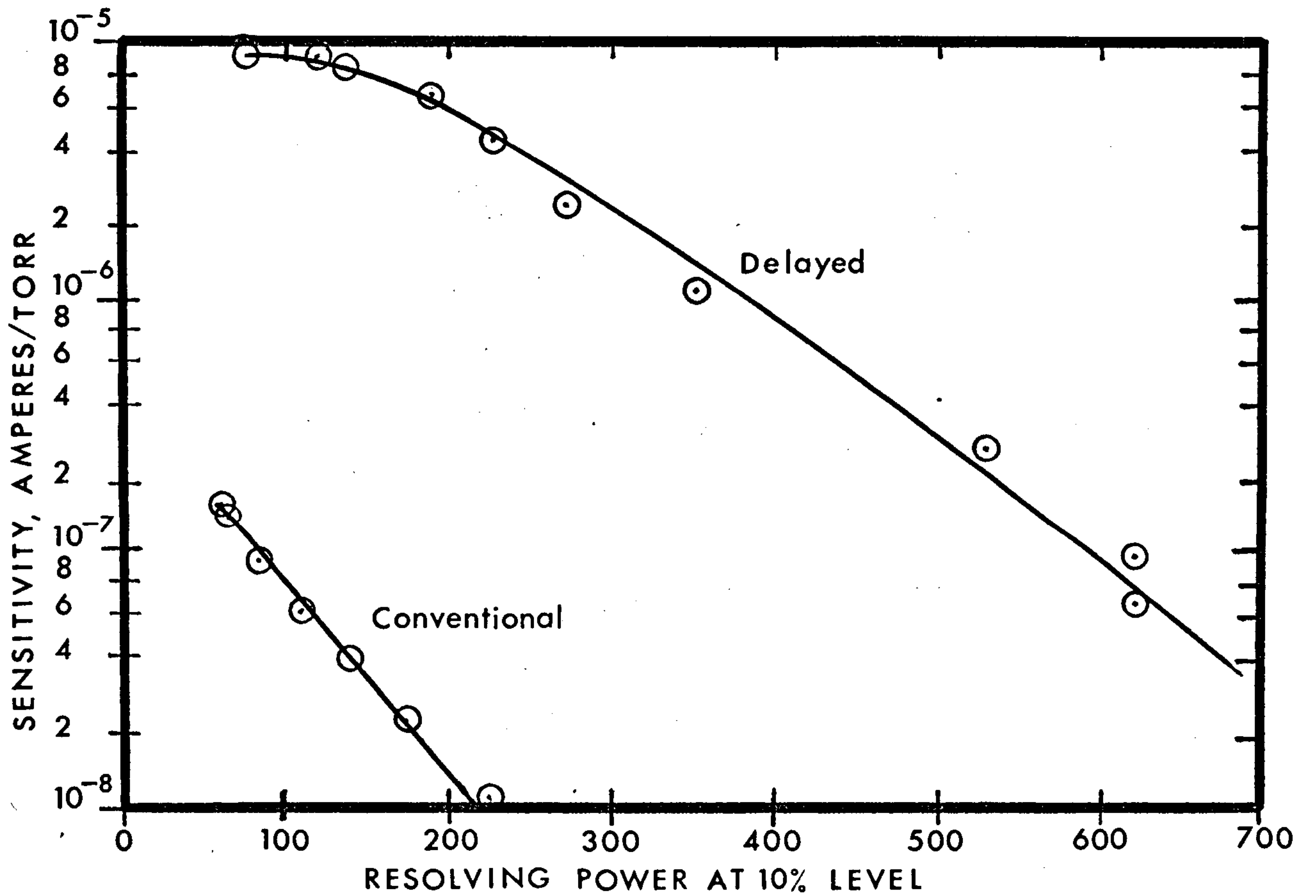


FIGURE 6

SENSITIVITY VS. RESOLVING POWER FOR CONVENTIONAL AND DELAYED MODES WITH 4-VOLT IONS